

S.N. 09/681,821

RD-26,970

Received 2/12/03
JCM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

:

J. C. Zhao et al

: Group Art Unit: 1775

Application No. 06/681,821

: Examiner: J. McNeil

Filed: June 11, 2001

: Response to Paper No. 4

For Diffusion Barrier Coatings, and
Related Articles and ProcessesDECLARATION OF PRIOR INVENTION UNDER 37 CFR 1.131

Ji-Cheng Zhao and Melvin R. Jackson declare:

We are the inventors of the invention claimed in the above-identified patent application. This declaration is to establish completion of the invention in this application, in the United States, at a date prior to March 24, 1999, which is the effective date of U.S. Patent 6,306,524 (Spitsberg et al). The referenced patent was cited by the Examiner in the Office Action of October 2, 2002.

We completed the invention in the United States prior to March 24, 1999. As proof of this statement, several exhibits are submitted herewith. Exhibit A is a patent Disclosure Letter written by us. At the time of the Disclosure Letter, we were members of the research staff of the General Electric Research and Development Center in Schenectady, New York. All acts described herein and in the exhibits were performed in the United States. Dates and irrelevant passages have been deleted from the exhibits.

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Page 1 of the Disclosure Letter generally describes the problems which can sometimes occur with aluminum diffusion between a substrate and a protective coating over the substrate. The consequential need for a diffusion barrier layer between the coating and the substrate is described in the last paragraph of that page.

Page 2 of the Disclosure Letter (e.g., section 2) describes the concept discovered by us, i.e., using a chromium-based material as a diffusion barrier layer. The various potential advantages of chromium over other barrier materials is also described on page 2. We also describe the application of such a layer to a nickel-based superalloy.

Page 3 of the Disclosure Letter describes other ideas we had in mind about some of the aspects of our invention. As an example, we describe the use of a barrier material like ours in a typical article, e.g., an airfoil for a gas turbine engine. We also describe a number of coatings that can be applied over the barrier coating, e.g., "MCrAl(X)"-type coatings, nickel-aluminide coatings, and, generally, coatings with relatively high concentrations of aluminum.

Page 3 also includes our signatures, and the dates of the signatures, although the latter have been deleted on this copy. The content of the Disclosure Letter was read and understood by two witnesses, who also affixed their signatures to the Letter.

Exhibit B is print-out of an electronic message from Ji-Cheng Zhao to Keith Borst, a technician working at Dr. Zhao's direction. The message was dated prior to March, 1999, although the date and irrelevant material have been deleted on the attached copy. The message directs Mr. Borst to prepare the compositions listed. Two of the compositions, designated

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as DB 30 and DB 32, are exemplary materials falling within the scope of our patent claims.

We further declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful, false statements so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful, false statements may jeopardize the validity of the application, or any patent issuing thereon.

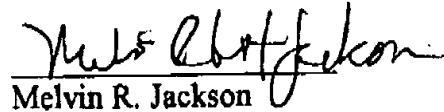
Ji-Cheng ZhaoDate: 1/17/03
Melvin R. JacksonDate: 1/17/03

EXHIBIT A - 3 PAGES



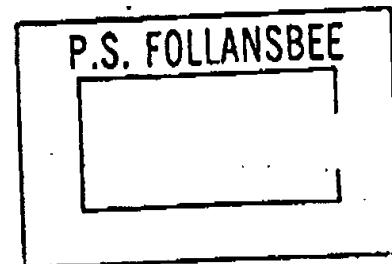
GE Corporate Research
& Development

Building K1-MB Room 231
Date:

Distribution:
Patent Operation (Original & 2 Copies)
Immediate Manager: Ann Ritter
Inventors: Ji-Cheng Zhao
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SUBJECT: PATENT DISCLOSURE LETTER
on: Diffusion Barrier Layer and Method of Making

1. **OBJECT OF INVENTION** (e.g., problem, opportunity, prior art)

There are two general classes of coatings that are currently used on gas turbine hot section parts including blade, nozzle, combustor, transition piece (duct), and so on. The first class is an MCrAl(X), where M is an element selected from the group consisting of Ni, Co, Fe and combinations thereof, and (X) is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, and C and combinations thereof. The second class is platinum modified nickel aluminide (Pt-NiAl), conventionally referred as Pt aluminide. Both of them have relatively high aluminum (Al) with respect to the superalloy substrate. At high temperature exposure, interdiffusion between the coating and the substrate can change the chemistry of the coating and the substrate and the chemistry of the oxide scale. Changes related to these interdiffusion processes affect not only coating chemistry, but microstructure, creep resistance, fracture toughness, phase composition and other coating properties, as well as growth of the alumina scale.

Essentially, there is a tendency for Al from the Al-rich aluminide outer layer to migrate inward toward the substrate, while traditional alloying elements present in the superalloy, Co, Cr, W, Re, Ta, Mo, and Ti migrate from the substrate into the coating as a result of composition gradients between the underlying superalloy and the coating. Extensive interdiffusion occurs between the coating and the alloy as a result of high temperature exposure. Aluminum diffusion toward the substrate reduces the concentration of Al in the outer layer, thereby reducing the ability of the outer layer to regenerate the highly protective and adherent alumina scale. Simultaneously, the migration of Co, W, Re, Mo, and Ti likely degrades the protective properties of the alumina. Another result of diffusion of Al is the formation of a diffusion layer or zone into the airfoil wall which essentially means undesirable consumption of the airfoil wall.

What is needed is a diffusion barrier between the coating and the substrate alloy that prolongs coating life by extending the time the coating chemistry provides a protective and adherent alumina scale, while being essentially chemically compatible with the bond coat and the superalloy, thermodynamically or kinetically stable and highly adherent to both the substrate alloy

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and the bond coat. In addition, the diffusion barrier should have low solubility and interdiffusivity for Al and elements from the substrate, minimal coefficient of thermal expansion (CTE) mismatch with the underlying substrate and the overlying protective coating, high stability at service temperatures, and ease of deposition preferably using currently available application techniques such as plasma spray, physical vapor deposition processes such as sputtering or other such methods. Oxide ceramics in which the diffusion rate of Al is low are likely candidates for diffusion barriers. However, these ceramic materials typically exhibit adherence problems.

Leverant patented (US Patent #5,556,713) a diffusion barrier using a submicron layer of rhenium (Re). As the turbine firing temperature increases, the interdiffusion between the coating and the substrate becomes more severe. A submicron layer of Re may not be able to effectively reduce or stop the interdiffusion between the coating and the substrate. Thicker layers of Re may spall during thermal cycling of gas turbine parts because of the CTE mismatch between Re and the superalloy substrate. In addition, Re can be oxidized rapidly to result in spallation of the coatings, which has been observed by GEAE in furnace cycle tests of test buttons sputtered with a pure Re diffusion barrier under a NiAl bond coat.

2. DESCRIPTION OF INVENTION

Instead of using refractory elements such as Re, we use Cr as a diffusion barrier layer. There are several advantages of a Cr diffusion barrier compared to a submicron layer of Re. First, Cr has a CTE very close to that of the superalloy substrate, thus a thicker, for instance 5 to 15 microns (rather than submicron in the Re case), more effective barrier layer can be applied without resulting in spallation. Second, Cr can be easily applied onto the superalloy substrate by electroplating method which is widely known in the art; electroplating is much cheaper and less time-consuming than physical vapor deposition (PVD) of Re. Third, Cr is beneficial to the oxidation and hot corrosion resistance of the superalloy and the Al-rich coatings, whereas Re is believed to be detrimental.

The solubility of Al in the body-centered cubic (bcc) Cr phase is very low, thus only very limited Al transport can occur across the diffusion barrier Cr layer. In addition, the interaction of Cr with refractory elements can form TCP phases that can tie up the refractory elements and can slow down the diffusion of these elements into the bond coat to degrade the coating performance. Therefore, a Cr layer can be an effective diffusion barrier layer for protective coatings.

3. OTHER INFORMATION (e.g., test data, reduction to practice, planned use)

As an example of this invention, we are testing a Cr diffusion barrier layer of ~ 5 micron thickness. The Cr layer was applied on Rene N5, a widely used Ni-based superalloy with a nominal composition by weight percent of 7.5 Co, 7.5 Cr, 6.2 Al, 6.2 Ta, 5 W, 3 Re, 1.5 Mo, 0.15 Hf, 0.05 C, 40 ppm B, 20-300 ppm Y and the balance Ni and incidental impurities. An NiAl bond coat was put on the Cr layer by electron beam vapor deposition (EB-PVD). The samples are TBC coated and further tests are in progress, including TBC & FCT test, interdiffusion study, microprobe analysis, and so on.

4. RECORDS AND REFERENCES

Tentative claims:

- An article for use in a high temperature oxidative environment, comprising: a nickel-base superalloy substrate; a Cr diffusion barrier layer with thickness between 2 to 20 microns; a coating having a high concentration of Al overlying the diffusion barrier layer.
- An airfoil for use in a gas turbine engine, comprising: a nickel-base superalloy substrate; a Cr diffusion barrier layer with thickness between 2 to 20 microns; a coating having a high concentration of Al overlying the diffusion barrier layer.
- A Cr diffusion barrier applied to a superalloy substrate by electroplating.
- The bond coat can be MCrAl(X), NiAl, Pt-NiAl, or any other oxidation and corrosion resistant compositions.
- The bond coat can be put on by various methods known in the art, such as electron beam vapor deposition (EB-PVD), ion plasma deposition (IPD), high velocity oxygen fuel (HVOF) deposition, air plasma spray (APS), vacuum plasma spray (VPS), low pressure plasma spray (LPPS), and so on.

5. INVENTORS, WITNESSES AND DATE

READ AND UNDERSTOOD BY:

Ann M. Ritter
Witness: Ann M. Ritter

Date: _____

*INVENTOR Ji-Cheng Zhao

Ji-Cheng Zhao

Advanced Materials & Processes Program
Physical Metallurgy Laboratory

Date: _____

READ AND UNDERSTOOD BY:

Charles G. Mukira
Witness: Charles G. Mukira

Date: _____

*INVENTOR Melvin R. Jackson

Melvin R. Jackson

Advanced Materials & Processes Program
Physical Metallurgy Laboratory

Date: _____

EXHIBIT B - 1 PAGE

AO-2-6170

-----Original Message-----

From: Zhao, Ji-Cheng (CRD)
Sent: 3:41 PM
To: Borst, Keith (CRD)
Subject: Target compositions

Keith,

Here is the composition of the DB alloy sputtering targets:

Alloy #	Designation	At.%								
		Ni	Cr	Ru	Al	Co	Ta	W	Re	Mo
DB30	CrRuAl		77	18	5					
DB32	CrReAl			65	5				30	

Thank you,

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Certificate of Transmission Under 37 CFR 1.8

I hereby certify that the correspondence listed below is being facsimile-transmitted to the United States Patent and Trademark Office on

Date February 12, 2003Receiving Facsimile Number: 703 872 9648

Correspondence:

Declaration of Prior Invention Under 37 CFR 1.131 (signed - 7 pages)

Application No. 06/681,821

Filed: June 11, 2001

Docket No. RD-26970

Signature


Francis T. Coppa